

The Bloom of Perovskite Optoelectronics: Fundamental Science Matters

In the past decade, halide perovskites (HPs) have gained enormous attention due to their rapidly advanced performance in solar cells, starting with a first reported power conversion efficiency (PCE) of 3.8% in 2009 to a certified 23.7% now.^{1,2} The exceptional performance of perovskite solar cells (PSCs) is attributed to the fascinating physical properties of HP materials such as long photocarrier diffusion lengths and large absorption coefficients, which also make HPs promising for a lot of other optoelectronic applications beyond solar cells (e.g., light-emitting diodes, photodetectors, X-ray scintillators). Recently, the HP community convened at the 2018 Materials Research Society (MRS) Fall Meeting (Nov. 26–30, 2018, Boston, MA, United States). The perovskite-themed “twin” symposia, ET04: *Perovskite Solar Cells — Challenges and Opportunities* and ET05: *Fundamental Aspects of Halide Perovskite (Opto)electronics and Beyond*, were among the busiest events of the MRS meeting with ~500 abstracts in total. The “twin” symposia also formed an unprecedented joint session “*The Past, Present, and Future of Halide Perovskites*” featuring five keynote speakers (David Mitzi, Tsutomu Miyasaka, Nam-Gyu Park, Anders Hagfeldt, and Kai Zhu) followed by a panel discussion on the most debated topics (stability, toxicity, upscaling, defects) in the perovskite field. The latest results and research trends of both fundamental and device aspects of HPs (see Figure 1) were intensely discussed and analyzed across the two symposia. Here, we present a brief summary of the highlights in both perovskite symposia, aiming to inform the perovskite and broader materials community of important ongoing developments and limitations regarding HPs for

greater exploitation of these fascinating optoelectronic materials.

Defect and Ions. Defect chemistry in a crystal lattice is what accounts for the difference between ideal and real crystals. The deviation from perfect crystallinity affects theoretical calculations and renders the underlying assumptions not completely applicable. Meanwhile, the impact of structural defects is enormous on basic material properties of perovskites and can appear in perovskite structures with different dimensionalities with the need for controlled passivation treatment. Filippo De Angelis highlighted some new results regarding defect/ion migration and polarons. In his work, he considered Frenkel defects as the major defect type expected in lead iodide perovskite structures. Electronic structure calculations suggested that large amounts of iodide anions exist at grain boundaries of perovskite materials, which thus indicated an increased ion migration and the principal surface locations of Frenkel defects. In addition, De Angelis showed that iodine interstitials can produce deep traps, which was verified by spectroscopic characterizations in collaboration with Annamaria Petrozza from Istituto Italiano di Tecnologia. Besides Frenkel defects, there are plenty of other possible defects in material lattices, such as linear, planar, or 3D bulk defects, with each defect requiring specific treatment for effective passivation. Nitin P. Padture demonstrated the importance of functionalizing the grain boundaries of perovskite methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$, or MAPbI_3) thin films via structurally incorporating triblock copolymer Pluronic P123. In the meantime, Xun Xiao adopted argon plasma treatment as an effective method to systematically control defects at the surface of perovskite films. In Xiao’s study, he concluded that only Pb^{2+} defects remained after argon plasma treatment, which made it highly targetable with specific passivation treatment. Profoundly, the argon treatment and surface passivation synergistically led to greater charge carrier mobility and thus consequently resulted in higher PCEs of solar cell devices. Moreover, Jacob Tse-Wei Wang introduced another passivation approach by coating a formamidinium chloride ($\text{HC}(\text{NH}_2)_2\text{Cl}$, FACL) layer on perovskite film. X-ray diffraction (XRD) measurements confirm that in the case of an additional layer of FACL the formation of PbI_2 can be prevented, while grazing incidence X-ray diffraction further confirmed that the FACL was not leaching into the perovskite bulk structure. The FACL crystallization on top of the perovskite layer resulted in less nonradiative recombination due to lower defect density. Therefore, a slower degradation process can be observed. Yabing Qi also touched upon the subject of Cl^- addition and showed an improvement of the PV

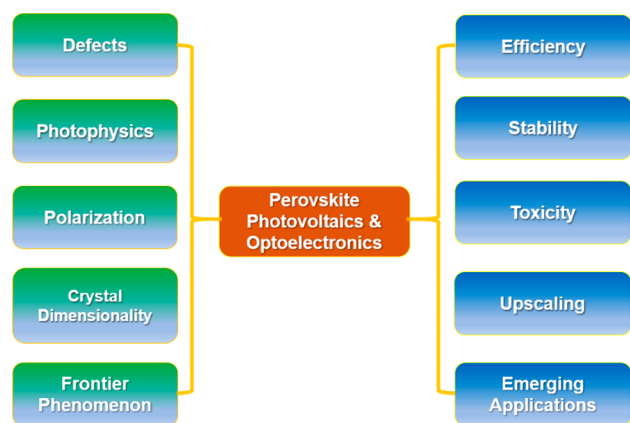


Figure 1. Key topics covered by the HP themed “twin” symposia, ET04: *Perovskite Solar Cells — Challenges and Opportunities* and ET05: *Fundamental Aspects of Halide Perovskite (Opto)electronics and Beyond* at the 2018 Materials Research Society (MRS) Fall Meeting.

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performance of solar cell devices with 1 μm thick perovskite layers upon treatment with Cl^- -doped hydrogen lead iodide and methylamine gas.³ Furthermore, a novel approach on defect healing was reported by Wallace Choy, where he used pulsed-dye laser treatment to enhance the performance of PSCs. In the meantime, David Cahen interpreted the uniqueness of HPs with respect to conventional inorganic semiconductors from the perspectives of material defects and structural disorders. Specifically, Yevgeny Rakita showed that the charge carrier mobility is intrinsically low for all soft crystalline materials including HPs. Joshua Choi further illustrated the significance of structural disorders by showing the strong impact of crystallographic orientation disorders on anisotropic electronic properties of HPs. Similarly, Andrew Rappe also mentioned the importance of structural dynamics and the role of lattice motions (ion diffusion and phonon modes) in affecting the excited-state charge carrier dynamics. In addition to the physical role of electronic properties, ion migration/diffusion also gives rise to chemical changes that severely deteriorate the stabilities of HPs. M. Saiful Islam presented in his work that rapid photodegradation can occur under the collective effects of I^- vacancies and O_2 diffusion in MAPbI_3 through superoxide (O_2^-) formation.⁴ These research results have again proved that HPs are mixed electron/ion conductors, and the halide defects play a significant role in the chemical stabilities of HPs. In fact, Alessandro Senocrate corroborated the ion-conductive nature of HPs through theoretical modeling that stressed the role of interstitial-type I^- migration in material lattices, which eventually leads to decomposition of perovskites. Other than I^- , MA^+ was also shown to diffuse across the material lattice, which could trigger reversible formations between MAPbI_3 and PbI_2 under the effects of external electric field, as unambiguously proved by Jinsong Huang. Juan Bisquert also indicated that ion drift can effectively suppress photoluminescence of HPs by generation of recombination centers. This is further substantiated in the talk by Samuel Stranks, who profoundly verified that many defects in HPs are by nature strain-related and are directly responsible for nonradiative recombination of charge carriers. Unlike the previous speakers who mainly studied I^- migration, Caleb Boyd pointed out that metal ion diffusion from device cathodes also concurrently takes place within PSCs. To effectively suppress this type of ion motion, Michael McGehee adopted ITO as a diffusion barrier for greater device stability.

Photophysics. Because the generation and fate of photo-carriers within HPs are extremely vital to the performance and properties of optoelectronic devices, Laura Herz provided photophysical insights to fundamentally account for these carrier processes. She pointed out the fact that band-to-band carrier recombination is simply the inverse process of photon absorption in the absence of Shockley–Read–Hall charge recombination, while the charge mobility is mainly dependent on the interplay between carriers and optical phonons. Meanwhile, Wolfgang Tress presented his research works on charge carrier recombination in PSCs, where he highlighted the pivotal role of open-circuit voltage in the reciprocal relationship between PV quantum efficiency and electroluminescence quantum yield. Furthermore, Xiaoyang Zhu demonstrated through experimental evidence that the liquid-like organic cation reorientation motions give rise to large polarons and ferroelectric polar domains in the materials, which are crucially responsible for the slow carrier recombination kinetics and exceptional defect tolerance. In addition to

the high performance in solar cells, HPs exhibit unusual electronic behaviors such as ferroelectricity, low-frequency giant dielectric response, and current–voltage hysteresis, in which ion motion has been widely thought to be the contributing factor. Aaron Walsh presented ion dynamics that govern the charge carrier processes in HPs, where he pointed out that the intermediate electron–lattice interaction regime is generally dominated by large polaron formation. Most importantly, Walsh mentioned that the large polaron states in MAPbI_3 exhibit distinctively slow thermalization kinetics, which should facilitate extraction of hot electrons for high-efficiency PVs.

Crystal Dimensionality. Being pioneers in studying low-dimension halide perovskites, Mercouri G. Kanatzidis and Lingling Mao demonstrated rich chemistry, tunable crystal structures, and exotic optoelectronic properties (e.g., high photoluminescence quantum yield, broad-band emission, etc.) in low-dimensional perovskites that include Dion–Jacobson (Figure 2a), Ruddlesden–Popper (Figure 2b), alternating

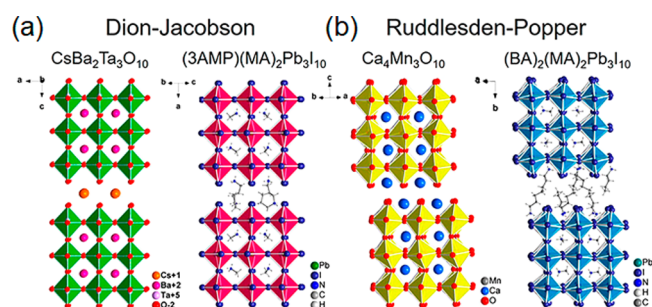


Figure 2. Schematic crystal structures of Dion–Jacobson-type 2D perovskites (a) and Ruddlesden–Popper-type 2D perovskites (b). Reproduced with permission from ref 13, copyright 2018 American Chemical Society.

cation and diammonium cation structural motifs. It is especially interesting to see that several papers related to the low-dimensional Dion–Jacobson-type HPs were published immediately after this meeting.^{9–11} Alternatively, Hemamala Karunadasa utilized double-perovskite $\text{Cs}_2\text{AgBiBr}_6$ for full substitution of lead while achieving long carrier lifetime. Moreover, by chemically incorporating butylammonium cations (BA^+), Karunadasa showed that double-perovskite $\text{Cs}_2\text{AgBiBr}_6$ also can transform into 2D layered systems, $(\text{BA})_4\text{AgBiBr}_8$ and $(\text{BA})_2\text{CsAgBiBr}_7$ with synergistic enhancement of stabilities, as widely recognized in BA^+/MA^+ co-cation perovskite structures when compared with 3D MAPbI_3 . Similarly, another great advancement in lead-free PSCs can be undoubtedly attributed to the titanium(IV)-based perovskites, which was reported by Min Chen, and Nitin P. Padture. Different from M^+/M^{3+} double perovskites (e.g., $\text{Cs}_2\text{AgBiCl}_6$), the new titanium(IV)-based Cs_2TiBr_6 perovskite has a vacancy-ordered crystal lattice. Most importantly, a good PCE of 3.3%, stable up to ~ 350 h under 70 $^\circ\text{C}$ and 30% relative humidity, was realized on an unencapsulated planar device by Chen.¹²

Materials and Device Stability. One of the intensely discussed topics during the symposium was the stability of perovskite absorbers. During the joint session of both symposia, when asked about thoughts on the instability issue on perovskite absorbers, Nam-Gyu Park considered that MAPbI_3 is sufficiently stable for long-term PV applications. Moreover,

Tsutomu Miyasaka even pointed out that PSCs based on MAPbI₃ are stable under simulated space environments with extreme temperatures and high-energy cosmic particle irradiations⁵ and therefore signify the suitability of MAPbI₃ PV panels in space applications. However, Satoshi Uchida indicated that MAPbI₃ thin films experienced degradations under electron beams of transmission electron microscopy, where the perovskite structure first amorphitized and then decomposed to PbI₂. The instability of MAPbI₃ was further agreed upon by Michael Saliba and Anders Hagfeldt, who stressed the need for symmetric A-site cations (e.g., Cs⁺, Rb⁺, HC(NH₂)₂⁺ (FA⁺)) for enhanced stabilities of HPs. Indeed, Saliba and Hagfeldt previously adopted mixed cation/halide perovskites as photoactive layers in solar cells to achieve phenomenal stabilities up to hundreds of hours under operational conditions with PCEs exceeding 20%. Although mixed I⁻/Br⁻ perovskites have notably greater stabilities as compared to pure I⁻ counterparts, they notoriously suffer from phase segregation problems, as agreed upon by Anthony Ruth who demonstrated through theoretical simulations that vacancies greatly promote I⁻/Br⁻ segregation under light conditions. Despite the divergent viewpoints toward stabilities of different HPs, Miyasaka and Hagfeldt unanimously mentioned that hole transport materials (HTMs) strongly affect the environmental stabilities of PSCs. In detail, polymer HTMs such as P3HT and PTAA lead to much greater device stabilities due to fewer pathways for moisture invasion (same motif as for the inverted p-i-n device architecture) and high structural robustness at elevated temperatures, as compared to conventional small-molecule spiro-OMeTAD. The subtle effects of HTMs were also corroborated by Luis K. Ono, who demonstrated that pinholes of spiro-OMeTAD layers (as generated by chlorobenzene solvent) accelerated degradation of PSCs. Likewise, other invited speakers of the joint session (David Mitzi, Laura Herz, Kai Zhu) emphasized that the detailed stability profiles of perovskite materials also highly depend on numerous critical factors, such as crystallinity, preparation routes/conditions, and/or physical encapsulation. In fact, Qingfeng Yan indicated in his talk that different crystallographic planes of MAPbI₃ single crystals exhibited anisotropic degradation kinetics under moisture conditions, where the (001) plane corrodes much faster than (100) and (112) planes.⁶ Such crystal facet-dependent moisture degradation effects clearly illustrate the crucial role of interfaces between water molecules and lattice arrangements and will effectively guide the fabrication of PSCs with preferred MAPbI₃ orientations for stable PV performance. Other than moisture stabilities, Annamaria Petrozza showed that light plays a complex role in forming and annihilating trap states in HPs with certain time scales by applying photoluminescence measurements and ab initio calculations, where suppression and formation of structural defects respectively dominate at short and long time scales. Although it is convincing at this point to infer that the stabilities of PSCs depend on specific cation compositions, environmental stress conditions, and structural interfaces of HPs, it is still unclear why the perovskite formulations with mixed cations/halides generally have much higher performance (PCE > 20%) than MAPbI₃ and α -FAPbI₃ PSCs.^{7,8} Edward Sargent and Hairen Tan pointed out that incorporation of small ions can release lattice strains without forming defects, and the mixed compositions can significantly suppress formation of vacancies. Furthermore, as Park emphasized in his talk, device interfaces play a vital role

in determining the PV performance and are becoming increasingly important for reaching the Shockley–Queisser limit (~33.7%) on PSCs. Substantially, Hagfeldt showed in his talk that by replacing Li⁺ in lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)-doped spiro-OMeTAD with Zn²⁺, the solar cell performance can be greatly improved.

Toxicity and Pb-Free Perovskites. Due to the toxicity problems, replacement of lead has become a vital topic in the research field of PSCs. Bert Conings stated the imminent necessity of pushing perovskite research into a lead-free field by assessing the general flammability and significant health risks from the combustion products of lead-based PSCs, even though commonly used concentrations of lead in PSCs seem to comply with regulatory limits. In response to the existing issue of lead toxicity, researchers focus on PSCs with tin-based HPs as the light-harvesting active layers. Nevertheless, tin-based PSCs only show efficiencies up to 9% while being plagued by poor stabilities due to oxidation of Sn²⁺ to Sn⁴⁺. Aslihan Babayigit indicated in her talk that SnI₄, which contains the undesired Sn⁴⁺, is already formed in perovskite precursor solution, while analysis of the precursor solution through UV–vis absorption can prevent the deposition of Sn⁴⁺-containing perovskite materials. To enhance the stability of tin-based perovskite, Weijun Ke doped diammonium cations (ethylenediammonium, propylenediammonium, or trimethylenediammonium) into perovskite structures for improved film morphology, notably higher PCEs, and greater air stability of fabricated solar cells. Remarkably, it was found that the oxidation of Sn²⁺ can be suppressed in mixed Pb²⁺/Sn²⁺ systems, as manifested in Gaurav Kapil's work. Kapil reported a high PCE of 20.4% as realized on solar cells with (Cs)_x(FAMA)_{1-x}Sn_{0.5}Pb_{0.5}I₃ as the perovskite absorber. The structure, oxidation states, and optoelectronic properties of (Cs)_x(FAMA)_{1-x}Sn_{0.5}Pb_{0.5}I₃ were unambiguously validated by XRD, X-ray photoelectron spectroscopy, photoluminescence, and transient absorption spectroscopy. Likewise, Shuzi Hayase and Min Chen achieved mixed Sn(II)/Ge(II) PSCs that were much more stable than pure Sn(II)-based cells due to the rapid facile oxidation of Ge(II) that formed a GeO_x surface oxide layer to protect the underneath Sn(II) composition. As a result of the native oxide passivation, Chen obtained a stable PCE of ~7% on a solar cell device with CsSn_{0.5}Ge_{0.5}I₃ as the light-harvesting layer.¹⁴

Upscaling and Commercialization. Deploying recent developments in industry is another crucial and challenging aspect of PSC research. Konrad Wojciechowski from Saule Technologies was invited to present the status quo of industrial approaches to PSCs, where an estimated timeline of commercialization was presented. Using a roll-to-roll slot die coating process, a highest efficiency of 13.5% could be stabilized on 16 cm² devices, as recorded by Pim Groen.¹⁵ So far, the measurements have only been carried out in an inert atmosphere, and the logical next step will be to conduct stability tests in air. Wojciechowski plans to start from initial pilot-line production of PSCs in the first quarter of 2019, and in 2020–2022 he plans further product development until they become acceptable to market. PSCs are of special interest for industry in terms of producing flexible substrates, which can be produced via printing or injecting via a cost-efficient way. Another desirable advantage of industrial production of perovskite PVs is that PSCs also work under low light conditions. Such a property points out new fields of use, such as building integrated photovoltaics (BIPVs). At Saule

Technologies, BIPVs have reached an efficiency of 10% to date.

Next Frontiers of Perovskite Research. The most frequent application of HPs other than solar cells can be attributed to LEDs. Due to large exciton binding energies as caused by strong quantum confinement, low-dimension and nanocrystal HPs successfully realized high-performance LEDs with high quantum efficiencies, as demonstrated by Li Na Quan, Dawei Di, and Jianjun Tian. Analogously, perovskites with low dimensionality and nanocrystal forms were simultaneously capable of achieving lasers with outstanding photoluminescence quantum yields, as noted by Qing Shen and Tzu-Pei Chen. Most of all, machine learning was systematically proposed to select phase-stable HPs for high-performance PSCs, as based on the boundary conditions of perovskite tolerance factors by Wanjian Yin. Such a practice was likewise performed by Marina Leite, who proposed the use of machine learning for monitoring the performance of solar cell devices. Additionally, HPs can be a new-generation materials platform for exploring quantum science and applications, which has been noted in some of the talks in the meeting and will be discussed in great details in Symposium ES17 at the coming 2019 MRS Spring Meeting (April 22–26; Phoenix, AZ).

In summary, the perovskite “twin” symposia at the 2018 MRS Fall Meeting were highly successful in addressing various challenges and opportunities of perovskite optoelectronics from different fundamental perspectives—defects/ion motions, photophysics, chemical stabilities, structural versatility, and emerging material properties. Newly discovered knowledge of HPs provides vital mechanistic guidelines for instructing the design of perovskite materials with greater stabilities and superior carrier properties and should therefore help approach the theoretical efficiency limits on PVs and other optoelectronics. Phenomenally, the increasing trend of adopting machine learning in designing perovskite absorbers signifies the promising potential of incorporating artificial intelligence in effectively screening for better photoactive materials. Most importantly, as exciting progress in lead-free perovskites was achieved owing to effective stability enhancements and defect passivations, commercialization of PSCs can be expected in the immediate future by collaboration with industrial partners while taking into account regulations, market needs, as well as implementation plans. The 2019 MRS Spring Meeting will continue the discussions of perovskite research in three symposia, ES15: *Fundamental Understanding of the Multifaceted Optoelectronic Properties of Halide Perovskites* (co-organized by Tze Chien Sum, Pablo Boix, Yabing Qi, and Carolin Sutter-Fella), ES16: *Perovskite Photovoltaics and Optoelectronics* (co-organized by Michael Saliba, Antonio Abate, Mingzhen Liu, and Yixin Zhao), and ES17: *Perovskite-Based Light-Emission and Frontier Phenomena—Single Crystals, Thin Films and Nanocrystals* (co-organized by Yuanyuan Zhou, Maria Antonietta Loi, Tingli Ma, and Iván Mora-Seró).

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Notes

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